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Short communication

Thermoelectric properties of screen-printed ZnSb film

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ABSTRACT

The thermoelectric properties of ZnSb thin film prepared by screen printing technique are investigated, aiming to achieve a low-cost and eco-friendly thermoelectric power generator module. The printed ZnSb thin film, annealed at 580 °C in a furnace tube achieves a power factor of 1.06 mW/mK^2 and a Seebeck coefficient of 109 μV/K. The output power density is 0.22 mW/cm^2 at $\Delta T = 70$ K. The feasibility of a flexible thermoelectric module using the screen printing technique is also demonstrated.

1. Introduction

Thermoelectric (TE) devices have potential for refrigeration and waste heat recovery applications due to their ability to accomplish direct conversion between thermal and electrical energies [1]. The latest thermoelectric research has mainly focused on improving the *ZT* of materials through material innovation or investigating low-dimensional structures to achieve phonon-glass and electron-crystal (PGEC) structures [2–6].

On the other hand, the high material cost incurred by using expensive rare materials such as tellurium (Te) is another challenge for large-scale application. Although TE modules are very attractive devices for renewable green energy applications, the high cost of fabrication and the limited amount of raw materials have been major hurdles for the wide usage of TE devices. In addition, Te, which is the most widely used material in current commercial TE modules, is a toxic material. Use of a toxic material for the basic element in TE modules makes it difficult to claim that it is a green technology.

In this work, we focus on the development of a low-cost and eco-friendly thermoelectric module for power generation. To realize a low-cost thermoelectric module, screen-printing technology has been applied to deposit thin-film thermoelectric materials.

2. Experimental details

The deposition of ZnSb thermoelectric films using screen printing technology requires five steps: paste synthesis, screen printing, leveling, drying, and annealing. The ZnSb paste was prepared by mixing the ZnSb powder, organic vehicle, and dispersant. The Zn and Sb powders have 99.0% purity and the size of the powder particles is 44 μm or below. The ZnSb powder mixing ratio was 50:50 (in atomic percentage) of Zn and Sb. The α-terpineol was used as the vehicle, and DisperBYK-110 as the dispersant. Ten grams of mixed ZnSb powder, 10 ml of α-terpineol, and 1 ml of DisperBYK-110 were thoroughly mixed for 24 h by ball-mill equipment. We then printed the ZnSb paste into a film on a SiO_2/Si wafer substrate by using a 325 mesh screen. The printed film was leveled for more than 10 min and dried at 100 °C in air for 10 min. Finally, it was annealed in a furnace tube or a rapid thermal processing (RTP) chamber. The annealing in a furnace tube was done by two-step annealing. First, it was annealed to remove the solvent at 300 °C for 20 min, and it was then annealed at higher temperatures for 10 min for the densification of the film. The thermoelectric module was also fabricated, using above mentioned ZnSb film and aluminum metal electrode by sputtering. The screen printed thin films were analyzed by field emission scanning electron microscope (FESEM, Sirion, operating voltage: 10 kV). The electrical and thermoelectric properties of the printed ZnSb film were measured using Keithley 2700 equipment, and the carrier concentration of the printed ZnSb film was measured using Hall Effect measurement system (HMS-3000, Ecopia).

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3. Results and discussion

The viscosity of the synthesized ZnSb paste was 0.2 Pa·s, and the thickness of the printed ZnSb thermoelectric film was about 30 μm in this experiment. The thickness of the printed film can be further increased, if necessary, by using a screen mask of smaller mesh size and repeating the printing until the target thickness is reached. Fig. 1 shows scanning electron microscope(SEM) images of the ZnSb film annealed at 500 °C (a) in a N_2 ambient using an RTP chamber and (b) in an air ambient using a furnace tube, respectively. The ramping rates of RTP and furnace annealing were 200 °C/min and 10 °C/min, respectively. The screen-printed ZnSb films are quite porous due to the evaporation of solvent during the annealing process. In particular, the film annealed using RTP is more porous than that annealed using the furnace tube, most likely due to the quick annealing and quenching effect in RTP. However, decreasing the ramping rate to lower than 10 °C/min does not improve the density of film. Although the screen-printed ZnSb thermoelectric film is porous, it shows reasonable thermoelectric properties. The thermoelectric properties of the screen-printed ZnSb film are shown in Fig. 2. The sample annealed in an RTP chamber has the maximum power factor of 0.285 mW/mK^2 at 500 °C, while the sample annealed in a furnace tube has the maximum power factor of 1.06 mW/mK^2 at 580 °C. Beyond these temperatures for each case, the power factor rapidly decreases and is too low to be plotted within the scale of the figure. Such a sudden degradation of the power factor at higher temperature annealing is believed to be due to the evaporation of Zn. The evaporation of Zn was evidenced by the fact that the semiconductor type of the sample was changed from p-type to n-type after annealing at a temperature higher than 600 °C. Note that furnace annealing provides a power factor 4 times higher than that provided by rapid thermal annealing. The difference in the power factor is probably caused by the difference in the carrier concentration as shown in Fig. 3. The maximum carrier concentration of the RTP-annealed sample is about one order of magnitude higher than that of furnace-annealed sample. Generally, a porous film provides a higher carrier concentration due to the high density of dangling bonds and other structural defects [7], and the RTP-annealed ZnSb film is more porous as shown in Fig. 1. An excessively high carrier concentration results in a low Seebeck coefficient and therefore a low power factor. These results indicate that the temperature ramping rate is a very important factor in the annealing of screen-printed thermoelectric films. Note that the previously reported power factor of bulk ZnSb material is in a range from 0.37 to 0.85 mW/mK^2 [8], which is comparable to the value obtained from the screen-printed and optimally annealed ZnSb film. This result is very encouraging and indicates the suitability of the screen-printing process for low-cost thin-film thermoelectric modules. In order to confirm such feasibility in a module level, a thermoelectric module was also fabricated. First, four parallel ZnSb legs were deposited by using screen printing on a SiO_2/Si wafer substrate and annealed at 500 °C for 10 min. Each ZnSb element has an area of 2.5 cm × 0.5 cm and a thickness of 26 μm. Aluminum layer was then deposited by using sputtering technique to connect ZnSb legs.

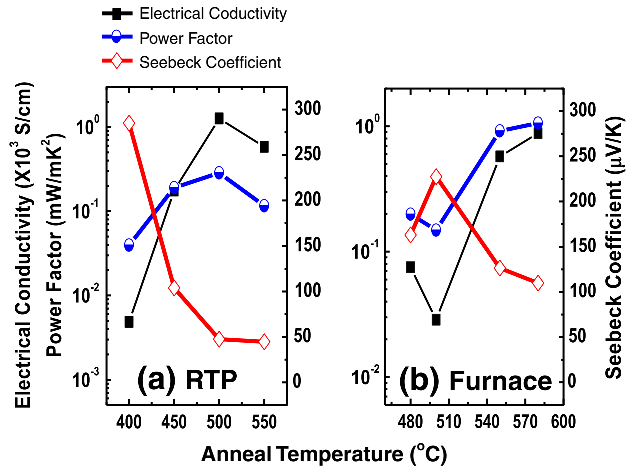

Fig. 2. Thermoelectric properties of screen-printed ZnSb film after annealing at various temperatures by (a) RTP and (b) furnace. The sample annealed in an RTP chamber has the maximum power factor of 0.285 mW/mK^2 at 500 °C, while the sample annealed in a furnace tube has the maximum power factor of 1.06 mW/mK^2 at 580 °C.

Fig. 4 shows the output characteristics of the simple ZnSb module. The electrical resistivity of the ZnSb measured using the module decreases with the operation temperature as shown in Fig. 4(a). The Seebeck coefficient also decreases with the temperature over the operating temperature range from 300 K to 530 K. Fig. 4(b) shows the output voltage of one ZnSb element of the module and the output power per unit area as a function of ΔT. In this measurement, the temperature gradient was given in a lateral direction, therefore ΔT in the figure is the temperature difference between the both sides of the module. The output voltage of one element increases almost linearly with ΔT, which is expected because both the electrical resistivity and Seebeck coefficient decreases together with the operation temperature as shown in Fig. 4 (a). The output power per unit area at ΔT = 70 K is 0.22 mW/cm^2 at a working temperature of 523 K. The output power is lower than that of commercial thermoelectric module using Bi–Te materials, because only a p-type material is used and not optimized module structure and fabrication process including electrode and contact processes. Nevertheless, the results presented in this work show the feasibility of using screen-printed ZnSb for low-cost-per-watt thermoelectric devices without using toxic and rare earth materials for eco-friendly renewable green energy.

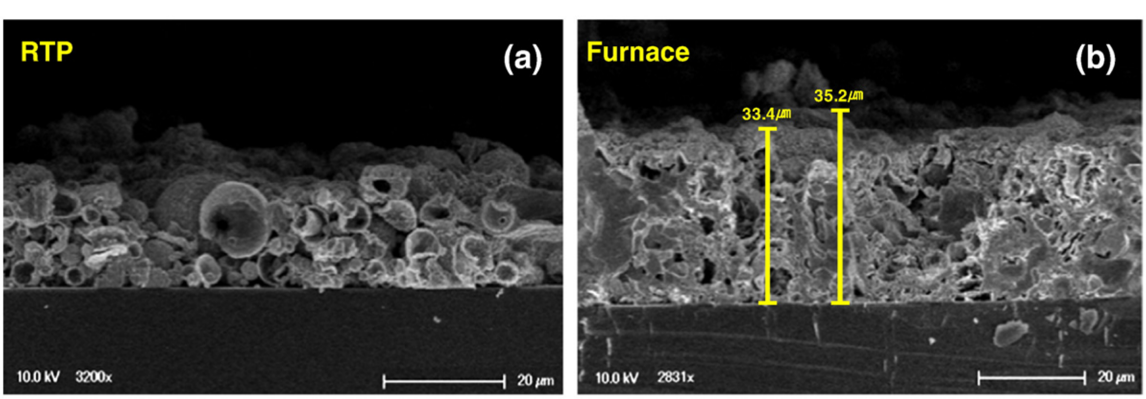

Fig. 1. SEM images of screen-printed ZnSb film after annealing (a) in a N_2 ambient using an RTP chamber and (b) in an air ambient using a furnace tube at 500 °C. The ramping rates of RTP and furnace annealing were 200 °C/min and 10 °C/min, respectively. The screen-printed ZnSb films are porous due to the evaporation of solvent during the annealing process and the film annealed using RTP is more porous than that annealed using the furnace tube.

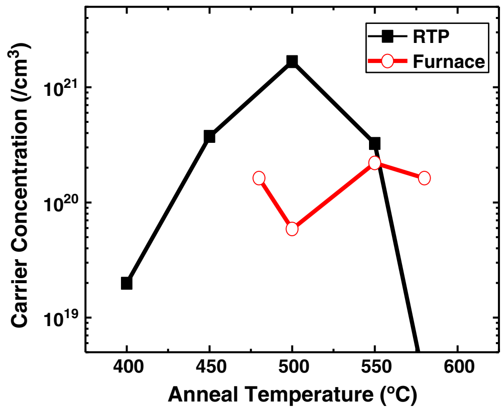

Fig. 3. Carrier concentration of screen-printed ZnSb film after annealing by RTP and furnace as a function of annealing temperature. The maximum carrier concentration of the RTP-annealed sample is about one order of magnitude higher than that of furnace-annealed sample.

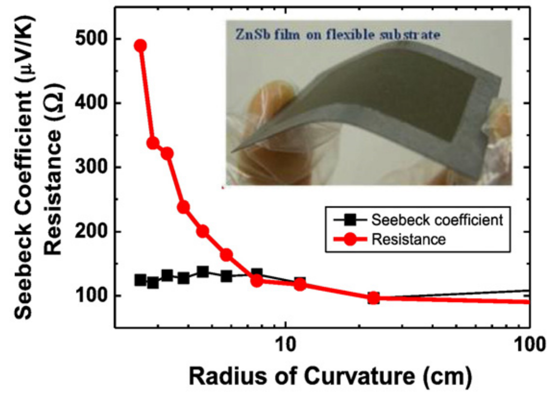

Fig. 5. Seebeck coefficient and resistance of ZnSb film as a function of radius of curvature. Photo in the inset is the fabricated ZnSb film on a flexible substrate. The Seebeck coefficient remains constant until the curvature radius is reduced to 1.5 cm, while the resistance remains constant down to a 7-cm curvature radius.

Finally, the ZnSb film was screen printed on a flexible substrate. Because of the porosity of the screen-printed ZnSb film, as shown in Fig. 1, it was expected that the screen-printed ZnSb would show good flexibility which would enables us to fabricate a flexible thermoelectric device. A Cu plate of 200 μm thickness was used as the flexible substrate. The Cu plate was oxidized for the purpose of electrical isolation, and then the ZnSb film was deposited on the Cu plate using the previously described screen-printing method. The sample was annealed at 500 °C for 10 min in a furnace tube. The thickness of the ZnSb film is about 31 μm. Fig. 5 shows the change of the Seebeck coefficient and the resistance of the screen-printed ZnSb film as a function of the radius of curvature when the substrate was bent. The Seebeck coefficient remains constant until the curvature radius is reduced to 1.5 cm, showing an excellent flexibility. However, the resistance remains constant down to a 7-cm curvature radius and then starts to increase, which will result in a decrease in the power factor. Therefore, at the moment, screen-printed ZnSb can be applied to a cylindrical heat source which has a radius of more than 7 cm, and we believe this can be further improved in the future by optimizing the thickness and the fabrication process.

4. Conclusion

To realize a low-cost eco-friendly thermoelectric module, screen-printing technology has been applied to deposit thin-film thermoelectric material. ZnSb film was prepared by a screen-printing method, followed by annealing for densification and the removal of organic vehicle and dispersant. It was found that the ramping rate is an important factor to determine the thermoelectric properties of the film and that furnace annealing provides better performance than RTP does. Through the optimal annealing process, the screen-printed ZnSb exhibited good thermoelectric properties which are comparable to those of bulk ZnSb, demonstrating the feasibility of using a low-cost screen-printing process for the fabrication of thermoelectric modules. The fabricated thin-film ZnSb also showed good performance on a flexible substrate, demonstrating its suitability for application in flexible thermoelectric devices, which is another advantage of the screen-printing technique.

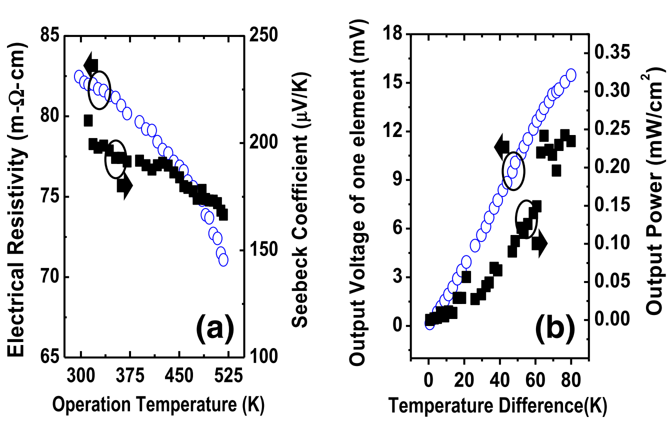

Fig. 4. Output characteristics of furnace-annealed ZnSb: (a) electrical resistivity and Seebeck coefficient as a function of operation temperature and (b) output voltage of one thermoelectric element and output power per unit area as a function of temperature difference. The output power per unit area at $\Delta T = 70$ K is 0.22 mW/cm^2 at a working temperature of 523 K.

Acknowledgements

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